

## AMENDMENTS TO THE SPECIFICATION

***Please replace the paragraph from lines 23 to 33 of page 11 with the following:***

In the present invention, unless stated otherwise, oil and water solubilities can be measured as follows: Hydrocarbon (oil) solubility may be measured as solubility in (i) model oils such as mineral spirits (a mixture of branched alkanes C<sub>9</sub> to C<sub>11</sub>, bp 179-210°C, available from Sigma-Aldrich Corp.), FINALAN<sup>TM</sup> 75 (a mixture of linear and branched hydrocarbons C<sub>10</sub>-C<sub>14</sub> plus a significant cyclic hydrocarbon content) or HALPASOL<sup>TM</sup> 190/240 (a mixture of n-alkanes C<sub>10</sub>, C<sub>12</sub> and C<sub>14</sub> and a minor concentration of branched hydrocarbons) or (ii) crude oil (i.e. which is typically from the formation in which the treatment fluid is to be injected).

***Please replace the paragraph extending from line 28 on page 14 to line 3 on page 15 with the following:***

Typical examples of preferred mutual solvents are dipropylene glycol methyl ether (DOWANOL<sup>TM</sup> DPM), ethylene glycol butyl ether (2-butoxyethanol; DOWANOL<sup>TM</sup> EB), and propylene glycol butyl ether (2-butoxy-propan-1-ol; DOWANOL<sup>TM</sup> PnB). Thus, for example, a mutual solvent may have a molecular weight of less than 300 g/mol, preferably less than 200 g/mol. Typically it has a molecular weight of greater than 50 g/mol.

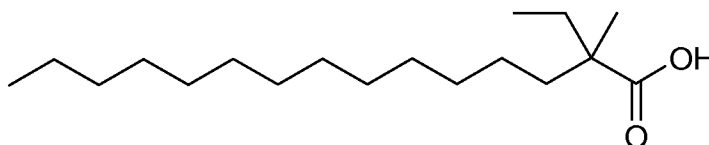
***Please replace the paragraph from lines 6 to 13 of page 17 with the following:***

This material is available from Resolution Performance Products who market the product under the tradename “VERSATIC<sup>TM</sup> 10” and from Exxon who market the product under the tradename Neodecanoic acid. At ambient temperature, neodecanoic acid (CAS reg. No. 26896-20-8) is a clear liquid; its density is 0.91kg/L at 20°C and its melting point is below -30°C. Calcium neodecanoate is commercially available from Strem Chemicals.

***Please replace the paragraph from line 18 to the bottom of page 17 with the following:***

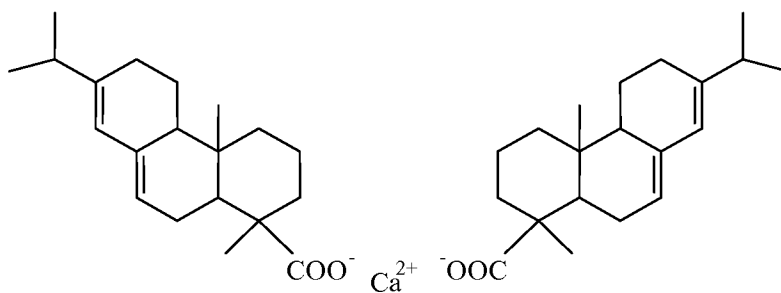
3. VERSATIC™ 10/18, a mixture of neo-C<sub>9</sub>H<sub>19</sub>COOH (VERSATIC™ 10) and neo-C<sub>17</sub>H<sub>35</sub>COOH (VERSATIC™ 18), supplied by Resolution Performance Products.

The probable structure of VERSATIC™ 18 is:



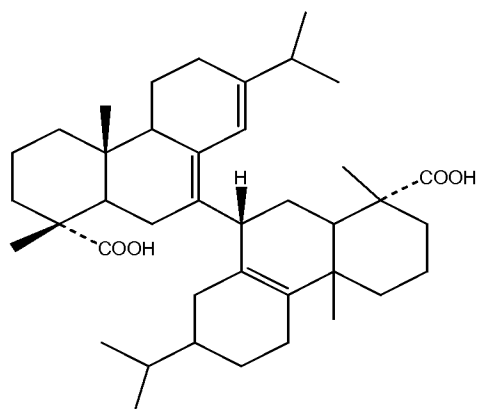
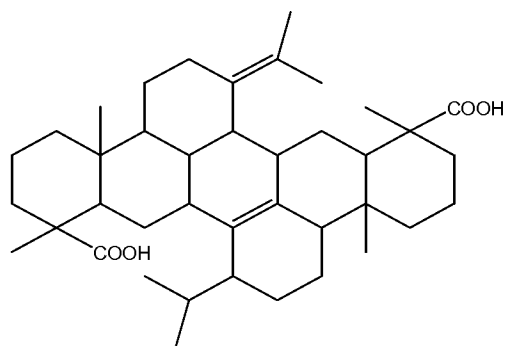
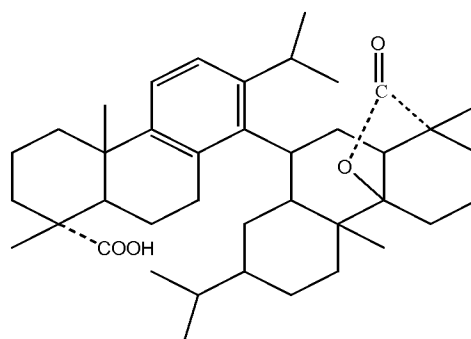
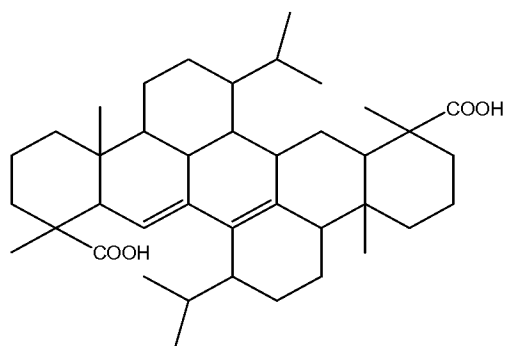
***Please replace the paragraphs at lines 4 to 13 of page 21 with the following:***

Calcium abietate, (C<sub>19</sub>H<sub>29</sub>COO)<sub>2</sub>Ca, is commercially available, for example, as the product “DERTOCAL™”, supplied by Les Dérivés Résiniques & Terpéniques S.A. or the product calcium resinate supplied by Barium & Chemicals, Inc. Calcium abietate is illustrated below:



Polymerised abietic acid may be used. This material is commercially available as the calcium/zinc salt, (C<sub>38</sub>H<sub>58</sub>(COO)<sub>2</sub>)<sub>n</sub>(Ca,Zn)<sub>n</sub>, for example, as the product “MERIGRAL™”, supplied by Les Dérivés Résiniques & Terpéniques S.A.

*Please replace the two chemical formulae at the top of page 22 with the following:*



***Please replace the paragraph at lines 10 to 22 of page 32 with the following:***

L is produced by reacting K with an alcohol R'-OH where R' is typically (OHCH<sub>2</sub>)<sub>3</sub>C-, OH-CH<sub>2</sub>-CH(OH)-CH<sub>2</sub>- or another polyol. Derivatives of non-phenolic resins can also be employed in the invention such as N, P and Q (see Figure 1). N and P are obtained as follows: G' (which is an isomer of G, see Figure 1) reacts with maleic anhydride to give M. M can then react with an alcohol R'-OH. When R' is (OHCH<sub>2</sub>)<sub>3</sub>C-CH<sub>2</sub>-, the product of the synthesis is N. When R' is OH-CH<sub>2</sub>-CH(OH)-CH<sub>2</sub>-, the product of the synthesis is P. Q is obtained by reacting G'' (polymerized abietic acid) with two molecules of penta-erythritol. The chemistry and synthesis of such resins and derivatives is described in detail in Zinkel and Russel. The water, solvent and oil solubilities of example phenolic-modified resin products (again available from Les Dérivés Résiniques & Terpéniques S.A. (DRT), 30 rue Gambetta – BP 206 – 40206 DAX Cedex (France)) are shown in Table 1; the commercial names of these products are RESENOL<sup>TM</sup> and GRANOLITE<sup>TM</sup>, (their likely structure is given by L in Figure 1).

***Please replace the paragraph from lines 23 to 32 of page 37 with the following:***

The divalent/trivalent metal carboxylate precipitates based on abietate or polymerised abietate are expected to be stable in strong acid as their parent acids, abietic acid or polymerised abietic acid are also oil-soluble, water-insoluble waxy solids with high melting points. In contrast, the divalent/trivalent metal carboxylates based on the  $\alpha$ -branched non-cyclic compounds, e.g. calcium neo-decanoate, are not expected to be stable in acid as the corresponding parent acid, neo-decanoic acid (VERSATIC<sup>TM</sup> 10), is a liquid at room temperature.

***Please replace the paragraph from lines 18 to 23 on page 38 with the following:***

Figure 2 shows the results of an experiment to compare the solubility at 25°C in di(propylene glycol) methyl ether (“DOWANOL™ DPM”) of 5 wt% calcium pivalate and 20 wt% calcium neo-decanoate. LEFT: 5 wt% calcium pivalate (prepared from VERSATIC™ 5); RIGHT: 20 wt% calcium neo-decanoate (prepared from VERSATIC™ 10).

***Please replace the paragraph at lines 6 to 11 of page 41 with the following:***

Figure 10 shows the result of an experiment to illustrate selective precipitation of a phenolic-modified resin (RESENOL™ 9070) from a treatment fluid consisting of 33wt% RESENOL™ 9070 dissolved in DPM. The addition of oil merely dilutes the treatment fluid, whereas the addition of brine causes the formation of a heavy waxy solid precipitate.

***Please replace the paragraph at lines 7 to 20 of page 42 with the following:***

The synthetic  $\alpha$ -branched saturated carboxylic acids, neo-C<sub>9</sub>H<sub>19</sub>COOH, neo-C<sub>12</sub>H<sub>25</sub>COOH and the neo-C<sub>9</sub>H<sub>19</sub>COOH/neo-C<sub>17</sub>H<sub>35</sub>COOH mixture are converted to divalent metal carboxylate salts by the following procedure. 500 mL of a 2 mol/L aqueous solution of NaOH is mixed with 200 mL deionised water in a 2 L beaker. Whilst continuously stirring the solution, 1 mole of the  $\alpha$ -branched carboxylic acid (e.g. 172.3g (189.1 mL) VERSATIC™ 10) is slowly added and then the volume of the solution is made up to 1 litre using deionised water. At this point, if necessary, the pH is adjusted to a value in the range 9–9.5. In this pH range, the solution should be clear as all the water-insoluble carboxylic acid has been converted to carboxylate anion:



*Please replace the paragraph at lines 3 and 4 of page 43 with the following:*

The dried calcium salt of VERSATIC<sup>TM</sup> 10 is a whitish waxy-crystalline solid.

**Please replace the text from page 43 line 20 to line 19 of page 45 with the following:**

For the case of abietic acid, calcium abietate (DERTOCAL<sup>TM</sup>), polymerised calcium abietate (MERIGRAL<sup>TM</sup>) and the phenolic modified resins (RESENO<sup>TM</sup> and GRANOLITE<sup>TM</sup>), insoluble residues were removed by filtration and the numbers given in Table 1 relate to the soluble fraction after filtration.

Table 1: Solubility of various calcium carboxylate salts in brine, oils and various solvents

Compound	Brine <sup>(1)</sup> wt%	Oil wt%	Solvent wt% (solvent chemistry)
*Ca Pivalate (VERSATIC <sup>TM</sup> 5)	5	0.01 <sup>(2)</sup>	2.0 (DPM <sup>(3)</sup> )
*Ca Decanoate (dry)	0.1	0.1 <sup>(2)</sup>	0.1 (EB <sup>(4)</sup> )
*Ca Decanoate (wet <sup>A</sup> )	0.1	0.1 <sup>(2)</sup>	0.1 (EB <sup>(4)</sup> )
*Ca neo-Decanoate (VERSATIC <sup>TM</sup> 10) (dry <sup>B</sup> )	0.5	0.5 <sup>(2)</sup>	<i>Glycol ethers:</i> ≥30 (DPM <sup>(3)</sup> ), ≥30 (EB <sup>(4)</sup> ), ≥30 (PnB <sup>(5)</sup> ). <i>Alcohols:</i> ≥30 (IPA <sup>(6)</sup> ), ≥30 (butan-1-ol), ≥30 (butan-2-ol), ≥30 (octan-1-ol), 0.5 (1,3-butanediol), <i>Ketones:</i> ≥30 (4-hydroxy 4-methyl 2- pentanone).
*Ca neo-Decanoate (VERSATIC <sup>TM</sup> 10) (wet <sup>C</sup> )	<0.83	≥5.8 <sup>(2)</sup>	≥10.8 (EB <sup>(4)</sup> )
*Ca neo-Decanoate (VERSATIC <sup>TM</sup> 10) (wet <sup>D</sup> )	<0.45	≥4.5 <sup>(2)</sup> , ≈4.5 <sup>(7)</sup>	≥6.8 (EB <sup>(4)</sup> )
*Ca neo-Tridecanoate (dry)	0.5	0.5 <sup>(2)</sup>	≥30 (EB <sup>(4)</sup> )
*Ca neo-Tridecanoate (wet <sup>E</sup> )	0.5	0.5 <sup>(2)</sup>	
**Ca Stearate	0.05	0.3 <sup>(2)</sup>	0.1 (EB <sup>(4)</sup> )
*Ca Oleate	0.3	0.5 <sup>(2)</sup>	1 (EB <sup>(4)</sup> )
*Ca Versatate 10/18 (wet <sup>F</sup> )	0.01	≥10 <sup>(2)</sup>	≥30 (DPM <sup>(3)</sup> )
**Ca Abietate (DERTOCAL <sup>TM</sup> )	0.01	>10 <sup>(2)</sup> ≥50.0 <sup>(7)</sup> ≥50.0 <sup>(8)</sup>	≥50 (DPM <sup>(3)</sup> ), ≥30 (EB <sup>(4)</sup> )
**Polymerised Ca/Zn Abietate (MERIGRAL <sup>TM</sup> )	0.01	>10 <sup>(2)</sup> ≥50.0 <sup>(7)</sup> ≥50.0 <sup>(8)</sup>	≥30 (DPM <sup>(3)</sup> ), ≥25 (EB <sup>(4)</sup> )
**Abietic Acid	0.01	≥6.5 <sup>(7)</sup> ≥5-10 <sup>(8)</sup>	≥30 (DPM <sup>(3)</sup> ), ≥30 (EB <sup>(4)</sup> )
**Camphor	very low	≥50.0 <sup>(7)</sup>	≥50.0 (DPM <sup>(3)</sup> )
**[(1S)-endo]-(-)-Borneol	very low	<9.0 <sup>(7)</sup>	≥50.0 (DPM <sup>(3)</sup> )
**RESENOL <sup>TM</sup> 9070 (Phenolic modified resin)	very low	≥11.0 <sup>(7)</sup>	≥35 (DPM <sup>(3)</sup> ), ≥35 (EB <sup>(4)</sup> )
**GRANOLITE <sup>TM</sup> 5758 (Phenolic modified resin)	very low	≥7.0 <sup>(7)</sup>	≥35 (DPM <sup>(3)</sup> ), ≥35 (EB <sup>(4)</sup> )

Footnotes to Table 1:

\*prepared as per procedure described in example 1.

\*\*commercially available: Ca stearate (Fischer Chemicals); Ca abietate, polymerized Ca/Zn abietate (Les Dérivés Résiniques & Terpéniques S.A.); abietic acid (Sigma-Aldrich Corp.); Camphor, Borneol (Sigma-Aldrich Corp.).

<sup>(1)</sup>brine = 1mol/L NaCl.

<sup>(2)</sup>Mineral spirits, bp 179-210°C (Sigma-Aldrich Corp.) – mixture of branched alkanes C<sub>9</sub> to C<sub>11</sub>.

<sup>(3)</sup>DPM: Dipropylene glycol methyl ether (DOWANOL™ DPM).

<sup>(4)</sup>EB: Ethylene glycol butyl ether (2-butoxyethanol; DOWANOL™ EB).

<sup>(5)</sup>PnB: Propylene glycol butyl ether (2-butoxy-propan-1-ol; DOWANOL™ PnB).

<sup>(6)</sup>IPA: isopropanol (propan-2-ol).

<sup>(7)</sup>HALPASOL™ 190/240 – mixture of n-alkanes C<sub>10</sub>, C<sub>12</sub> and C<sub>14</sub> and minor concentration of branched hydrocarbons.

<sup>(8)</sup>FINALAN™ 75 – mixture of linear & branched hydrocarbons C<sub>10</sub>–C<sub>14</sub> plus a significant cyclic hydrocarbon content.

<sup>A</sup>55wt%water   <sup>B</sup>3wt%water   <sup>C</sup>17wt%water   <sup>D</sup>55wt%water   <sup>E</sup>55wt%water   <sup>F</sup>20wt%water

Note: when carboxylate salt is in a wet state, the quoted solubility is active (dry) weight percentage dissolved.

***Please replace the paragraphs at lines 6 to 22 of page 47 with the following:***

The commercially available abietic acid, calcium abietate, polymerized calcium/zinc abietate and phenolic modified resins show a very low solubility in water, high solubility in glycol ether solvents and high solubility in oil. The composition of the oil will affect the solubility of these compounds and it is known that aromatic oils are also good solvents for these compounds (e.g. DRT report that DERTOAL™ 140 and MERIGRAL™ CB are soluble to 50wt% in toluene).

Figure 2 compares solubility of calcium pivalate and dry calcium neo-decanoate in di(propylene glycol) methyl ether (Dow Chemical DOWANOL™ DPM) at T=25°C. The bottle on the left in Figure 2 contains 5wt% calcium pivalate (prepared from VERSATIC™ 5), and its contents



appear white, showing that the calcium pivalate salt has not dissolved. The bottle on the right contains 20wt% calcium neo-decanoate (prepared from VERSATIC™ 10), and its contents appear colourless and transparent, with no visible precipitate.

***Please replace the paragraph at lines 8 to 13 of page 49 with the following:***

Further examples of the selective response to increasing dilution with oil or brine are provided by equivalent tests performed using treatment fluids containing calcium neo-tridecanoate, calcium versatate 10/18, abietic acid, calcium abietate (DERTOCAL™) and polymerized calcium/zinc abietate (MERIGRAL™). A summary of the tests is given in Table 2.

***Please replace Table 2 on page 50 with the following:***

Table 2: Selective behaviour of candidate treatment fluids in well-mixed bottle tests

Dissolved calcium carboxylate salt	Solvent	Behaviour on dilution with brine	Behaviour on dilution with oil (mineral spirits)
10wt% Ca neo-decanoate	Pure DPM	Pptn. when [brine]=67vol%	No pptn., one clear phase
5wt% Ca neo-decanoate	50vol%DPM/ 50vol%brine	Pptn. when [brine] increased from 50 to 70vol%	No pptn., two clear phases
10wt% Ca tri-decanoate	Pure DPM	Pptn. when [brine]=70vol%	Two clear phases but light ppt. at interface
10wt% Ca versatate 10/18	Pure DPM	Pptn. when [brine]=33vol%	No pptn., one clear phase
5wt% Abietic Acid	Pure DPM	Pptn. when [brine]=33vol%	No pptn., one clear phase
5wt% Ca abietate (DERTOCAL™)	Pure DPM	Pptn. when [brine]=23vol%	No pptn., one clear phase
5wt% polymerized Ca/Zn abietate (MERIGRAL™)	Pure DPM	Pptn. when [brine]=5vol%	One clear phase but light ppt. formed after 12 hr.; when oil is FINALAN™ 75, no ppt. observed.

***Please replace the paragraphs at lines 6 to 13 of page 51 with the following:***

The phenolic modified resins also have high melting points (e.g. RESENOL™ 9070: 170°C; GRANOLITE™ 5758: 180°C).

Interestingly, both calcium abietate and abietic acid have high melting points indicating that both the calcium and acid forms will form a stable precipitate in reservoirs with a broad temperature range. In contrast, whilst their calcium salts have high melting points, VERSATIC™ 10, VERSATIC™ 10/18 and tridecanoic acids are all liquids at ambient temperature.

***Please replace Tables 4 and 5 on page 59 with the following:***

Table 4: Examples of mutual solvents

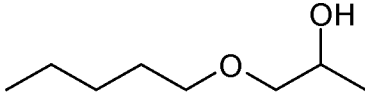
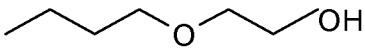
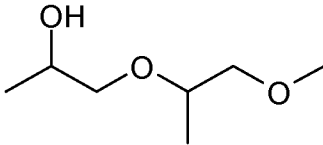
Solvent		Structure
IUPAC name	1-butoxy-3-propanol	
Common name	Propylene glycol monobutyl ether	
Abbreviation	DOWANOL™ PnB	
IUPAC name	2-butoxyethanol	
Common name	Ethylene glycol monobutyl ether	
Abbreviation	DOWANOL™ EB	
IUPAC name	1-(2-methoxyisopropoxy)-2-propanol	
Common name	Dipropylene glycol methyl ether	
Abbreviation	DOWANOL™ DPM	

Table 5: Details of mutual solvents

Name (abbreviation - see Table 4)	DOWANOL™ PnB	DOWANOL™ EB (U66)	DOWANOL™ DPM
Formula	C7H16O2	C6H14O2	C7H16O3
Melting point (°C)	<-80	-74.8	-83
Boiling point (°C)	171	168.4	188.3
Flash point (°C)	63	65	75
Density (g/cm <sup>3</sup> )	0.879	0.902	0.953
Deionised water solubility (wt% at 25 °C)	5.5	100	100
HLB number <sup>1</sup>	6.88	7.35	8.18
Hildebrand parameter <sup>2</sup> (cal/cm <sup>3</sup> ) <sup>1/2</sup>	9.3	10.2	9.6